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Method and apparatus for treatment of pulp

The present invention relates to a method and an apparatus for treatment of pulp. The method and the apparatus according to the invention are particularly well applicable to treatment of chemical pulp by using chlorine dioxide in a treatment phase in which the use of chlorine dioxide has been optimized.

It is a known fact from the prior art that about two decades ago cellulose fiber suspension was still bleached mainly with elemental chlorine Cl_2 . This was done by mixing into the pulp elemental chlorine which had been absorbed into cold water, max. temperature 20 °C. Then the bleaching process was allowed to continue at a low LC consistency (typical consistency about 3 - 4 %) at a temperature of 20 - 40 °C for about 60 min. In the 80's the use of chlorine started to be reduced mainly due to environmental reasons because the AOX content of effluents had become an important criterion in the protection of environment and the AOX emissions could be reduced most efficiently by replacing elemental chlorine with chlorine dioxide in the bleaching.

It was found out already in the 1940's than chlorine dioxide, ClO_2 , which in every-day language is called dioxide, is a usable chemical in the bleaching of pulp and in fact the only chemical used at that time with which sulfate pulp could be bleached to the full brightness of over 86 - 90 % (ISO). Thus it was natural to use these chemicals originating from chlorine, i.e. both elemental chlorine and chlorine dioxide, side by side in successive treatment stages and later on in the same treatment stage to improve the quality of pulp. From this time comes also the practice of performing the bleaching process containing chlorine at a relatively low temperature. Using chlorine the pulp mills had learned that a suitable bleaching temperature is approximately the room temperature because chlorine gas dissolved in water evaporates at higher temperatures and the process cannot be controlled. One reason for the difficulty in the control of the process was the lack of efficient mixing methods. Until the 1970's, mixing of large chlorine volumes into the pulp was successful only in a water solution at a low consistency because the operation of chemical mixers was fluctuating and the mixing results were crucially different from each other in different processes.

The problem caused by the mixing of chemicals was practically solved when the high-intensity fluidizing mixers became available on the market and they were introduced both into MC and LC bleaching stages. At the same time it became possible to use chlorine in
5 gas form instead of elemental chlorine in water solution, the gas being dissolved directly into the liquid in the pulp suspension and reacting there with the pulp without a separate dissolving process. At its best the whole chemical dose could be consumed efficiently during the process because of the efficient mixing.

10 Mixing is an important stage in the bleaching of pulp, which ensures that there is an even chemical consistency around each fiber. Mixing of chlorine dioxide into the chlorination stage was considered advantageous in view of the pulp quality and at the same the temperature of the chlorination stage could be raised as, due to the efficient mixing, all the chemical was consumed very fast and evenly, and the addition of dioxide was
15 considered to protect the pulp from quality losses at the high temperature.

As the leading trend ever since the 70's has been to close the processes and to reduce the volume of effluents, the use of a higher temperature in the C, C/D and D₀ stage has provided benefits for the heat economy of the mill. As mills were provided with modern
20 biological effluent purification plants, it became necessary to start performing the bleaching stages at the MC consistency, as the operation of the purification plants required an essential reduction in the volume of water and an increase in the concentrations. Finally, for environmental reasons the use of chlorine was given up and the first typically delignifying electrophilic bleaching stage was transformed into a mere
25 dioxide stage, i.e. the so-called D₀ stage.

In other words, the temperature of the chlorine dioxide bleaching stage used as the first stage in a bleaching sequence has been raised very slowly, in pace with the withdrawal of prejudice so that today the normal treatment temperature at the MC consistency stages
30 varies within a wide range of the order of 45 - 70°C. Not until recently, around the middle of the 90's, the delignifying dioxide bleaching D₀ has been suggested to be performed at a higher temperature, i.e. at a temperature close to 100 degrees or even

higher, in which case a completely pressurized process is used in order to prevent the water in the fiber suspension from boiling. However, in all cases the risk of deterioration of the pulp quality has been experienced. In the process technology in general, raising the temperature results in acceleration of chemical reactions and thus faster consumption of chemicals, and as a detrimental property when dioxide is used, an increase in the volume of chlorine-containing exhaust gases. Further, at the high temperature of over 90°C, the danger of corrosion in the presence of chlorine-containing liquid increases. Also, the temperature of over 90°C is difficult in view of the heat economy of the mill.

Chlorine dioxide treatments are, because of their chemical character, divided in the bleaching sequences into two different stages each having their own purposes and process conditions. The so-called D₀ stage is a delignifying treatment stage, the main purpose of which is to decrease the Kappa number of the pulp and the main reaction of which has been described in the wood chemical publications as an electrophilic stage. As publications discussing the subject are mainly more than ten years old the literature does not deal with a mere D₀ stage but a combined CD stage is discussed, i.e. chlorination utilizing dioxide combined with elemental chlorine. The D₁ and D₂ etc. stages in the subsequent bleaching sequences are brightening stages which aim at increasing the brightness of the pulp and the chemical reaction of which is mainly nucleophilic. This has a different chemical character and totally different control parameters have influence on it than on a D₀ stage. Literature (e.g. Pulp and Paper Manufacture, Volume 5, Alkaline Pulping, Tappi 1989) very clearly recommends, in particular for bleaching dioxide stages, a temperature of 50 - 90°C and a treatment time of more than two hours. The nucleophilic (brightening) and the electrophilic (delignifying) dioxide stage are separated in the literature based on the pH so that the former has a pH range of 1.8 - 4 and the latter a pH range of 3 - 6.5. Patent literature, however, mentions pH ranges of up to 8. The pH ranges mentioned overlap to some extent as the pH changes when the treatment stage proceeds and as the pH is adjusted according to the number, i.e. two or three, of the dioxide stages in the bleaching.

Controversial views on the optimal conditions of a D₀ stage have been presented in many contexts and it has not been possible to give flawless grounds for the optimal conditions.

In practice, bleaching has mostly been carried out at a pH of 1.8 - 3.5, preferably 2.2 - 3, at a temperature of 45 - 60°C and with a retention of about ½ - 1 hours but it has not been possible to prove that a rise in the temperature even nearly always results directly in quality losses. Controversial views on the optimal conditions may be partly due to the development of mixing techniques. The D₀ stage may have worked differently even in the same mill due to different mixing efficiencies. In our studies we have proved that the chemicals are consumed very quickly and the change of temperature within a small range does not as a whole have as a remarkable effect on the quality of pulp as has been thought.

The dosing of chlorine dioxide into the treatment stage has been controlled by state of the art methods so that a sensors have been provided in the feed duct from the mixer to the reactor, which both measure the residual chemical and indicate the pulp brightness and the feed of the chemical has been controlled based on the information given by the sensors. The amount of the chemical needed in the treatment stage has been adjusted with the apparatus but from time to time interpretation of the information given by the sensors has been found problematic due to the varying process conditions. For technical reasons the measurement has been performed after a retention time of less than half a minute after the mixing of the chemicals itself at which time in the prior art processes typically 30 - 60 minutes of the retention of the whole bleaching treatment is still left. Thus it is clear that the residual chemical measured after a very short retention after the mixer is indicative and does not give a comprehensive picture of the proceeding of the bleaching reaction or its speed.

The studies we have performed have shown that if the mixing of the pulp is efficient enough the chemical can be totally consumed in the chlorine dioxide stage in a short reaction time and at a remarkably lower temperature than is suggested by the kinetic model (Chlorine Dioxide Delignification Kinetics and Eop Extraction of Softwood Kraft Pulp, The Canadian Journal of Chemical Engineering, Volume 75, February 1997) which has recently been accepted in general discussion. In the tests we have performed, the chlorine dioxide mixed into the pulp was completely consumed in a few minutes already at a temperature of 60°C when the mixing was adequately efficient. The same kind of

result were received from the treatment of pulp in tests in both one stage and in several stages. An efficient laboratory reactor was used in all the test. Although the temperature could not be proved to have a direct correlation with the decrease of the Kappa number, the chemical residue and the brightness of the pulp in this connection, its significance as a factor accelerating the reaction is known from prior art installations and the basic chemical literature and it has been proved also in other laboratory tests. Based on the tests, it is clear that the temperature need not be over 85 - 90°C in order to have a quick reaction. Thus, the kinetic model mentioned indicates a slower chemical consumption than it really is if the chemical is dosed using efficient mixing. The study leading to the kinetic model in question has been made in laboratory conditions and probably the test have not been made with modern laboratory reactors used now allowing fluidizing mixing. Thus in the kinetic model of the test, the reaction kinetics is limited by the mixing because the significance of the mixing has not been taken into account. Thus it can be concluded that raising the temperature, increasing the mixing efficiency and increasing the retention will compensate each other.

EP-B1-0 496 782 discusses D₁ and D₂ stages which are brightening, nucleophilic treatment stages. According to the publication these stages are performed in two steps from which the first at a pH of the order of 6.0 - 10.0 and with a mixing time of 5 - 40 minutes and the second step at a pH of 1.9 - 4.2 and with a treatment time of two hours or longer. The temperature in both the steps is about 55 - 85°C. The purpose of the two-step treatment described in the publication is to achieve a higher brightness with a certain chlorine dioxide dose than before or to achieve the same brightness with a smaller dioxide dose. In the treatment stage according to the publication chlorine dioxide need not necessarily be added to the second step at all but according to the publication also a low pH achieved by acidifying is adequate for the result desired.

SE-C2-504 210 deals with a multistage bleaching process in which chlorine dioxide is used in at least one stage. According to the publication, the chlorine dioxide stage is performed at a temperature of 90 - 130 degrees, at a pressure of 0.1 - 10 bar, at a consistency of 8 - 40 %, and with a retention time of 1 - 90 minutes. According to the publication, the pressurized dioxide stage mentioned is suitable for both the beginning

and the end of the sequence. The method described in this patent publications is based on a study made by Sunds Defibrator Industries AB, which is also discussed in the article "Advancing the Chlorine Dioxide Process", Nordén & Mellander, The 12th Sunds Defibrator International Technical Seminar, May 29. – 31. 1996, Sundsvall. The starting point of both the article mentioned and the patent publication is that the advantageous treatment time is 15 minutes or longer. Thus the reaction kinetics of the method described in the patent publication and the article mentioned corresponds to the kinetic model presented in the study mentioned above when the kinetic model is calculated for the temperature 90 - 130°C discussed.

WO-A-98/00602 deals with a multistage bleaching sequence which uses as a starting point the dioxide stage described in patent SE-C2-504 210. This stage has been continued without an intermediate wash in a way by another treatment step in which the treatment pressure and the temperature of the pulp in a down-flow tower have been reduced whereby the chlorine dioxide residues in the pulp are separated to the gas phase of the down-flow tower and can be removed from there.

The prior art publications mentioned above disclose thus both the hot and the pressurized dioxide stage, as well as a two-step chlorine dioxide stage, in which only a short retention and mixing time do not suffice, even if it is intended particularly for a bleaching stage. The publications also partly aim at reducing the volume of chlorine dioxide to be used and at intensifying the bleaching process. However, these goals are striven for only by raising the temperature and by arranging the bleaching stage two-stepped. All the processes cited above have the typical feature that either the dioxide stage is very long, of the order of more than 30 minutes, or the stage is very hot and pressurized in which case the high temperature and the pressurization is considered to allow the use of a little shorter reaction time. However, none of the publications suggests performing the first chlorine dioxide treatment following the brown stock washing or oxygen bleaching with a treatment time if a few minutes at a known low temperature when the pH is between 2 and 4 at the beginning of the treatment and between 2 and 3 at the end of it.

The studies we have performed have shown, however, that prior art methods have several weak points which may be improved and thus the operation economy of the chlorine dioxide stage may be brought to a quite new level. These prior art methods do not for example pay attention to the significance of mixing as an accelerator of the reaction, or at least it has not been systematically reported, and on the other hand the temperature has not been used as an active parameter in controlling the consumption of chemical. Further, in the prior art solutions the dioxide treatment has been carried out based on laboratory tests performed with low-intensity mixing; thus the influence of the mixing has not been understood. On the other hand, even when fluidizing mixers have been used, the meaning of the mixing efficiency they provide has not been understood and made fully use of.

The main objective of the present invention is to minimize the consumption of chlorine dioxide without compromising the efficiency and the result of the treatment.

Another objective is to reduce the size of the equipment needed in the D_0 stage and thus to reduce the investments of the mill. Prior art D_0 stages have been performed with a relatively long treatment time which requires a fairly large treatment tower which in turn requires space and in particular increases investment costs as, because of the corroding effect of chlorine dioxide, the tower must be constructed of titanium or a corrosion resistant special steel, provided with brick lining.

A third objective is to improve the process technical controllability of the stage, whereby the pulp is subjected to contact with the chemical only in conditions in which the bleaching chemical is used in the reaction, and to raise the temperature only as much as is required to adjust the bleaching reaction to last only as long as the pulp needs to flow from the mixer to the discharge of the reaction vessel. Thus the reaction can be adjusted actively with the temperature.

A fourth objective is to optimize the ratio of the mixing needed and the reaction volume so that, by ensuring efficient mixing, the bleaching reaction is completed at the temperature of 50 - 85°C and at the same time to prevent high temperatures which are unfavorable in view of the heat economy. The objective is to reduce the corrosion risk of

the stage by using a low temperature. The temperature is of essential importance also because with the temperature rise the treatment of exhaust gases becomes problematic. Temperatures below 90 degrees allow using indirect heating methods.

- 5 A fifth objective is to minimize, in the recycling of filtrates, the contact of the pulp with the reaction products in order to avoid harmful by-reactions. Tests we have performed show that chlorine dioxide is consumed in by-reactions for example with the organic substance in the fiber suspension coming to the dioxide stage D₀ either from the brown stock washing or the oxygen stage. In other words, chlorine dioxide does not only react
10 with the lignin of the fibers but also with the organic matter in the liquid phase of the suspension.

- A further objective is to reduce the amount of toxic chlorinated phenol compounds which are, as is known, produced during the dioxide treatment. It has been found out that these
15 phenol compounds are produced when the dioxide reacts with the organic matter produced during the treatment or present in the fiber pulp. In other words, when reacting with the organic matter dissolved in the liquid phase of the fiber suspension, chlorine dioxide forms these chlorinated phenol compounds. Our invention relates to a treatment method in which the reactions of the chlorine dioxide with the organic by-products of the
20 liquid phase, i.e. with the organic matter measurable with the COD, are minimized.

- In order to reduce the environmental load of a pulp mill, it is specifically desirable to reduce the volume of effluent from the bleaching process. Many industrial prior art installations have ended up in using the apparatus arrangement illustrated in Figure 1.
25 However, already when deciding on the apparatus arrangement it has been known that recycling the reaction products from the washer subsequent to the treatment tower with the filtrate back to the pulp suspension will reduce the brightness of the pulp at the end of the bleaching stage and increase the consumption of chemicals during the bleaching. This has been established also in our test, in which pulp was treated with recycled filtrate and
30 clean water. When bleaching with recycled filtrate, the brightness of the pulp in the D₀ stage was reduced by 2 - 5 % (ISO) brightness units compares with pulp diluted with clean water.

Similar results were received also by the authors of the kinetic model cited above in their experiment, in which the brightness of the pulp began to drop in the first chlorination/chlorine dioxide stage after a certain time. According to the study, the
5 highest brightness level was reached exactly at that moment when the chemical had been completely consumed in the conditions of the test. As only reactions products of the stage remained in the pulp suspension, the detrimental impact of the reaction product of the D₀ stage on the development of the brightness was easy to see. The same applies both to the reactions products originating from the recycling and to the reaction products,
10 which remain in the pulp when reactions cease as all the chemical has been consumed.

These two studies, i.e. our own and the external study, indicate that both the time the pulp stays in contact with the reaction products and the amount of the reaction products are detrimental to the development of the brightness. In order to solve this problem, the
15 retention of the dioxide stage, i.e. the time from the chemical feed to the subsequent wash of the pulp, should be adjusted to be only as long as is necessary for the reactions of the lignin, i.e. until all the bleaching chemical has been consumed, and the bleaching should be stopped when the chemicals have been consumed. In this way the time the pulp is in contact with the effluent of the bleaching is minimized and thus the bleaching losses are
20 reduced to the minimum. In practice, the detrimental by-reactions take place a little after the main reaction as the by-reactions require the presence of reaction products in the liquid phase. When the main reactions with the bleaching chemical can be actively controlled by adjusting the temperature, also the amount of the detrimental by-reactions, i.e. the time available for these reactions can be reduced to a minimum. This is essential
25 always in a D₀ stage but it is of particular importance when the original pulp has been diluted with filtrate obtained from the same D₀ stage. In order to minimize the drawbacks of this recycling, the retention of the D₀ stage must be adjusted short.

The studies we have performed have shown that a D₀-E bleaching of pulp, in which the E
30 is an alkaline stage, and the use of a short dioxide stage and intensive mixing in the presence of filtrate produces a brightness level can be reached which is very close to the level reached with bleaching processes using clean water. As the brightness has

developed well in the presence of the reaction products of the D₀ stage, shortening the treatment time of pulp also reduced brightness losses in a stage where reactions products of the bleaching stage are present. This is natural as tests have proved that a prolonged reaction time drops the brightness when all the chemicals have been consumed.

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Tests we have performed have also shown that the organic matter originating from the oxygen stage require a certain bleaching chemical content to cause the bleaching chemicals to be consumed in the oxidation of the organic matter. In our tests this consumption of chemicals practically stopped altogether when the chemical content in the liquid was 2 g/l active chlorine. Thus, the dioxide content should be kept relative low, if the consumption of the bleaching chemical in reactions with the organic matter of the filtrate is to be reduced. If necessary, chlorine dioxide may be dosed into the pulp at several stages. Then the chlorine dioxide content in the liquid phase remains relatively low and the dioxide reacts with the lignin compound in the pulp, only. Among other things these goals have been reached in a bleaching stage, in which the treatments have been chained so that the chlorine dioxide is dosed into the pulp in several steps if necessary and the similar treatment of pulp is repeated successively several times. Although retention time must be allowed between the treatments, the retention required to consume the chemical to an adequate degree may be only a few seconds depending on the conditions.

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It was already stated above that the dioxide stage retention from the chemical feed to the subsequent wash should be only long enough to allow the dioxide to do what it used for, i.e. to react with the lignin in the pulp. This is because it has been found out that the quality of pulp deteriorates if the pulp is too long in contact with the reaction products. However, the state-of-the-art dioxide stages have been constructed so that the pulp is discharged from a dioxide tower to an atmospheric space which may be a drop leg, a tank or a corresponding member in which the pulp is diluted if required and from which the pulp is pumped further to a washer. This retention allows the pulp to continue reacting with the reaction products and consequently the quality of the pulp degrades.

A characteristic feature of a preferred embodiment of the invention is that it, among other things, solves the problem described above by arranging the dioxide stage washer as close to the dioxide reactor as possible. Experiments have shown already that pulp can be fed with the dioxide stage pump through the reactor straight up to the washer as the consumption of chemicals is very fast and the reactions can be controlled well.

This procedure, however, involves a new problem. When a washer is brought close to the dioxide reactor it must be ensured that no harmful amounts of dioxide end up in the washer because of the corrosion hazard caused by dioxide. Depending on the material of the washer, some dioxide may be allowed in the pulp flowing to the washer; in other words, the amount of the dioxide allowed depends on the materials used. It is possible to determine both experimentally and based of studies for each material the allowable residual dioxide level, which secures adequate life.

Thus, because of this problem, it is necessary to make sure that either there is no dioxide left in the discharge of the reactor, that the dioxide can be eliminated from the pulp leaving the reactor, or that the dioxide amount is acceptable in view of the material of the subsequent apparatus.

There are several solutions to this problem. In principle these are divided into two groups: ways to make sure that there is no dioxide in the pulp discharged from the reactor, and ways to eliminate dioxide from the pulp discharged from the reactor. Solutions in the first group mentioned are for example selecting the reaction temperature, reaction time and reactor size so that the dioxide has time to react well before the pulp is discharged from the reactor. Naturally, this is facilitated by mixing the dioxide with pulp as efficiently as possible, i.e. by using a fluidizing, in other words high-intensity mixer.

The second group involves destroying the dioxide discharged from the reactor with the pulp before the pulp is fed to a washer. The destruction of dioxide is usually performed by mixing chemical, in most cases sulphur dioxide water or sodium bisulphate into the pulp which reacts with the chlorine dioxide producing inert compounds which are easy to remove from the pulp during the wash. An essential feature in carrying out the process of

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our invention is that the chemical is mixed with the pulp very efficiently. The purpose is to distribute the chemical into the pulp so that it can react with the residual dioxide as fast as possible, i.e. before the pulp comes to the washer. Thus, the invention covers both measured aiming at fast consumption of chemicals and destroying the residual chemicals
 5 prior to the washer, which provides for the use of short retention times reliably and without risk.

Other characteristic features of the method and apparatus of the present invention are disclosed the in appended patent claims.

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The methods and the apparatus of the invention according to the invention are described more in detail below with reference to the accompanying drawings of which

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Fig. 1 illustrates schematically the apparatus arrangement of a process simulated in our tests;

Fig. 2 illustrates the change in the brightness of the fiber suspension in different bleaching stages determined based on our studies, as a function of the number of filtrate recycles;

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Fig. 3 illustrates the COD content of the fiber suspension liquid phase in different bleaching stages determined based on our studies, as a function of the number of filtrate recycles;

Fig. 4 illustrates the COD content of the fiber suspension liquid phase in different dioxide concentrations determined based on our studies, as a function of the number of filtrate recycles;

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Fig. 5 illustrates apparatus for carrying out the chlorine dioxide treatment according a preferred embodiment of the invention; and

Fig. 6 illustrates an apparatus arrangement for carrying out the chlorine dioxide treatment according another preferred embodiment of the invention.

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Fig. 1 illustrates schematically the apparatus arrangement of a process simulated in the tests, comprising a washing apparatus 10, a press, a washer or a corresponding member, and illustrating the practical situation in which an essential portion of the water and the reaction products originating from digestion or oxygen bleaching is removed from the

- pulp coming from a preceding treatment stage, i.e. either from screening and washing following the digestion or additionally also from oxygen bleaching or ozone treatment, which all are in the following called brown stock. After the washing apparatus 10, particularly if the washer is a press, the pulp is diluted at point 12 to the MC consistency before it is guided to a mixer 16. Further it is advantageous to heat the pulp to a desired temperature before the mixer. The pulp can be heated either by using the wash water of the washing apparatus 10 or after the washing apparatus by appropriate means. The heating can be carried out for example directly with the dilution liquid, in a separate feed tank or with a separate steam heater 14, preferably by means of direct steam heating or by heating the wash liquid of a preceding washer. Also chlorine dioxide can be mixed into the heated and diluted pulp in the mixer 16. The mixer 16 may also be used for mixing into the pulp alkali or acid in order to adjust the pH of the pulp to be appropriate for the treatment. In addition to heating the pulp before the mixer 16, the pulp may be heated in some cases alternatively after the mixer 16 if desired for example with an indirect heat exchanger. After the dilution, heating, preferably steam heating, if they have been desired, and the mixing of chlorine dioxide the pulp is guided to a treatment vessel 18, from which the pulp is further taken to a wash apparatus 20, preferably at the pressure of the apparatus feed pump (not illustrated).
- As was already stated above, it must be ensured that no dioxide causing corrosion is brought to the washer with the pulp. This is ensured for example by providing the discharge end of the reactor with a discharger by means of which chemical is mixed into the pulp to eliminate dioxide from the pulp. The discharger must have an adequately high intensity so as to reach absolutely even distribution of the chemical into the pulp. Preferably the apparatus comprises a apparatus containing a fluidizing means, whereby the mixing of chemical takes place in a fluidized state. However, there are also static high-intensity mixers available with which fluidization can be reached in a narrow slot. Other mixing devices may be for example a valve provided in the discharge of the reactor or in the vicinity of it, which, when throttled under an adequate pressure difference (>1.0 - 1.5 bar), fluidizes the pulp to a state which fully corresponds to the mixing obtained with a prior art fluidizing mixer provided with a rotating mixing member. Also a fluidizing discharger may be used as the mixing member, which has been provided with means, for

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example vanes, for increasing the pressure. In some cases, it is also possible to use a fluidizing pump, for example a so-called MC pump, both for mixing the chemicals and for pumping pulp to a washer.

- 5 In other words, the apparatus of the invention comprises a pump, from which pulp is pumped to a reactor, which due to the short reaction time may be a relatively short duct, a mixer placed preceding the pump if dioxide is not mixed in the pump, a mixing apparatus disposed substantially at the discharge end of the reactor vessel or in the vicinity of it and mixing the chemical which eliminates the dioxide, and a washer. The essential feature of
- 10 the apparatus described is that pulp travels from the dioxide mixing to the washer in a closed space and thus chlorine-containing compounds are prevented from escaping to the atmosphere.

- When studying the invention the apparatus illustrated in Figure 1 was simulated in a
- 15 laboratory by introducing to dilution 12 continuously a pulp batch the properties of which correspond to the ones of pulp obtained conventionally from brown stock washing. Here brown stock means, as was stated above, chemical pulp which has been washed and screened, or washed, screened and bleached with oxygen, or washed, screened and treated with ozone. As brown stock washing is typically performed with a press, the pulp was
- 20 brought to the dilution at the discharge consistency of the press, which is typically about 30 %. After the first dilution with clean water to the consistency of about ten percent, chlorine dioxide was added to the pulp under vigorous mixing substantially during the whole time the dioxide was added. Finally, the pulp was bleached in laboratory equipment and the filtrate separated while thickening the pulp was returned from the
- 25 wash, which corresponds to the washer 20 in Fig. 1, to be used as dilution liquid in the new pulp batch to be bleached, which procedure corresponds to the dilution 12 after the washing apparatus 10. As particularly the wash filtrate during the continuous recycling was to be studied, a sample was taken from the wash filtrate from each cycle, and the amount of organic solids in it was determined by an analysis depicting it, i.e. by the so-
- 30 called COD (mg/l). Quite a number of these bleaching processes were performed by recycling the filtrate of the washer in the way described above. It was found out that the recycling of the filtrate from the bleaching decreased the bleaching result by several

brightness units whereby the presence of reaction products in the D_0 stage results in decreasing of the bleaching result at the end of the sequence (Fig. 2). The sequence D_0 -EP- D_1 was used in the experiment.

5 Figure 2 illustrates the decrease in the final brightness as a result of the increase in the amount of reaction products in the bleaching sequence D_0 -EP- D_1 . The horizontal axis in the figure illustrates how many times the filtrate from the washing stage ending the D_0 stage was recycled back to the dilution preceding the D_0 stage. The figure illustrates how the recycling times of the filtrate, i.e. in this case how many times there are reaction
10 products from the D_0 treatment present in the bleaching stage, decrease the brightness of the pulp and thus creates needs to increase the amount of the chemical required in order to reach the desired brightness. Since the retention is the same in each bleaching, the concentration of the reaction products from the bleaching has a significant role in the decrease of the brightness in this case. Figure 2 further indicates that the increase in the
15 volume of reaction products does not affect strongly the brightness after the D_0 stage but only the brightness after the EP and D_1 stages which at its worst decrease by more than 10 ISO units.

Figure 3 illustrates the increase of COD as a function of the number of recycling times in
20 a three-stage D_0 -EP- D_1 bleaching when all the stages have been simulated as illustrated in Fig. 1. In other words there has been no intermediate wash of the pulp but filtrate has been pressed out from the pulp and the pulp has been diluted for the following stage with filtrate obtained from the following stage mentioned by pressing it out from the previous pulp batch. It should be noted that the COD content increases in the D_0 stage in the liquid
25 phase remarkably but does not increase much with the number of the treatment times; thus, dioxide oxidizes and consumes in the D_0 stage the organic matter which is measurable with the COD analysis. This means that in the conditions prevailing in the D_0 stage, chlorine dioxide oxidizes non-selectively the organic matter both in the pulp and in the filtrate. In other bleaching stages the phenomenon is not as remarkable and the
30 increase of the COD content continues in the liquid phase for a longer time. On the other hand, the increase of impurities in the liquid phase reduces the final brightness reached.

Figure 4 illustrates how filtrate from an oxygen stage, i.e. brown stock treatment, has been treated with chlorine dioxide solution under bleaching conditions. The results indicate that when the concentration of the bleaching chemicals at the beginning has been very high, the bleaching chemical has reacted with the COD of the filtrate so that the COD of the filtrate has not increased almost at all irrespective of the number of the recycling times. This is illustrated by the lowest of the three curves in Fig. 4. On the other hand, the tests showed that when the concentration of the bleaching chemical in the filtrate was 2 g/l calculated as active chlorine the chlorine-containing chemical is almost not at all active with the filtrate of the oxygen stage but the COD content of the liquid phase can rise relatively freely (the topmost curve). The third curve in Fig. 4 illustrates the chemical concentration of 2.5 g/l calculated as active chlorine and it can be seen that the COD content already rises to some extent, i.e. in practice the activity of the chlorine chemical relative to the filtrate of the oxygen stage has reduced remarkably. This speaks for arranging the chlorine dioxide stage so that the concentration of the bleaching chemical is not allowed to rise much over 2.5 g/l in the filtrate during one treatment stage or step.

Thus, the present invention also relates to different ways of running bleaching processes according to a preferred embodiment of the invention so that the dioxide concentration in the fiber suspension to be treated remains less than 2.5 g/l, preferably less than 2.0 g/l calculated as active chlorine. The test we have performed have indicated that the treatment time in the reaction vessel should be shorter than 10 minutes, preferably shorter than 7.5 minutes, more preferably shorter than 5 minutes. According to our tests the temperature of the pulp should be over 40°C whereby naturally the temperature and the treatment time are inversely proportional to each other, i.e. when the temperature is high the treatment time can be shorter and vice versa. The pH in turn should be 1.5 - 5.5, preferably 2 - 4.

Another test aiming at determining the limit for the chlorine dioxide concentration is presented in table 1.

Table 1Original solution: O₂ stage solution, COD 14800 mg/l

Results from chlorine dioxide treatment of solution

| dosed active Cl, g | solution ml | at end active Cl, g/l | COD at end |
|-----------------------|----------------|-----------------------------|---------------|
| 0.3 | 500 | 0.24 | 14800 |
| 3 | 500 | 1.85 | 10700 |
| 6 | 500 | 2.02 | 7300 |
| 9 | 500 | 1.93 | 5600 |

The test presented in the table was performed by dosing 0.3 - 9 g/l chlorine dioxide calculated as active chlorine into filtrate from an oxygen stage the COD content of which was 14800 mg/l. Finally, both the COD and the amount of residual dioxide were determined. The results indicate that with a dioxide dose of 3 g/l and more, the COD of the solution has reduced and still the amount of residual dioxide has remained at 2 g/l. In other words, also this test supports the theory presented earlier that the dioxide concentration calculated as active chlorine should be less than 2.5 g/l, preferably less than 2.0 g/l, in order to prevent the dioxide from being consumed in undesirable reactions with the COD.

Example 1

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The following table presents the chlorine dioxide bleaching tests performed with a short bleaching stage D₀-EP the results from which have been determined always after a similar alkaline extraction stage. A laboratory reactor provided with high intensity mixing and automatic dosing equipment has been used in tests 1 -7. Only for the comparison, the results from a corresponding bleaching test performed in a plastic bag with low intensity mixing are presented (test 8). After the tests the residual chemical content was always determined from the pulp in order to make sure that all the dioxide had been consumed in

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the bleaching reactions in all the tests.

Table 2D₀ stage

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Consistency 10 %, amount of softwood pulp 135 g, Kappa 16.7, Viscosity 1108,
Brightness 35.5

| | Code | Injection Dilution | | Temp °C | D dose kg/adt | Time min | Kappa (after E stage) | Visco | Brightness |
|----|------|--------------------|----------------------|------------|------------------|-------------|--------------------------|-------|------------|
| 10 | 1 | 100% | water | 60 | 38.41 | 5 | 3.2 | 1027 | 57.4 |
| | 2 | 100% | water | 70 | 38.41 | 5 | 3.3 | 1036 | 57.2 |
| 15 | 3 | 100% | water | 85 | 38.41 | 5 | 3.4 | 1030 | 57.7 |
| | 4 | 50+50 | water | 70 | 38.4 | 3+3 | 3.3 | 1019 | 57.2 |
| 20 | 5 | 50+50 | water | 85 | 38.41 | 3+3 | 3.4 | 992 | 58.1 |
| | 6 | 50+50 | D ₀ clean | 70 | 38.41 | 2+2 | 3.3 | 1007 | 55.3 |
| | 7 | 50+50 | D ₀ clean | 85 | 38.41 | 3+3 | 3.5 | 964 | 56.4 |
| 25 | 8 | 100 | water | 60 | 38.41 | 45 | 4.0 | 1042 | 57.9 |

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In tests 1 - 3, clean water was used as dilution liquid, 38.41 kg/adt of chlorine dioxide calculated as active chlorine was dosed all at the same time under intensive agitation, the treatment time was 4 - 6 minutes and only the temperature was changed in order to find out the influence of the temperature increase on the end result. As can be seen from the results, the influence of the temperature on the brightness or the Kappa number of pulp is not significant. In fact, the differences both in the Kappa numbers and the brightnesses determined between the tests remain within the limits of measurement accuracy.

Tests 4 and 5 were performed otherwise the same way as described above except that the dioxide was dosed at two stages so that the treatment time in both stages was three minutes. When the temperature was changed, no essential changes were detected in the Kappa number and also the changes in the brightness remained under one ISO unit.

In tests 6 and 7, filtrate from a dioxide treatment was used in the dilution, the chemical was dosed in two stages and the treatment time in both the stages was in test 6 two minutes and in test 7 three minutes. Between the test, the temperature was raised from 70 degrees to 85 degrees. Still the Kappa number and the brightness remained practically unchanged. It is worth noticing that neither a treatment time, which was 50 % longer, nor a temperature, which was 15 degrees higher, did bring a clear improvement in the results in test 7.

Test 8, which was performed in a plastic bag, corresponds primarily to test 1, compared with which the only difference in addition to the chlorine dioxide mixing method is that the treatment time, 45 minutes, used in the test is the time given by the kinetic theory for a dioxide treatment performed at the temperature of 60 degrees. The results indicate that the Kappa number remains a little weaker than in the tests 1 - 7 performed applying the method of our invention. On the average the same brightness was reached as in the tests simulating our tests.

It may be concluded from the tests that it is possible to make all the chemical (chlorine dioxide) to be consumed by using intensive mixing at a remarkably shorter time than is suggested by the kinetic model, and in a test series performed at a temperature below 85 – 90 °C, quality losses measured with viscosity (scan standard method) are not significant and are mainly due to prolonged mixing occurring in the laboratory equipment.

Example 2

130 g pulp having a consistency of 10 % and a Kappa number of 29.7 was supplied to the laboratory reactor used in the test 1 – 7 of example 1. 60 kg/adt chlorine dioxide calculated as active chlorine was mixed into the pulp, the pulp was mixed well and the reaction was allowed to continue for three minutes at a temperature of 60°C. After this the residual chlorine was determined from the pulp; it was 0.2 kg/adt. In other words, more than 50 % larger dose of dioxide than used in tests of the previous example was practically all consumed in three minutes.

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Based on the test in example 2, it can be expected that it is possible in industrial scale to treat brown stock with chlorine amounts of the order of 70 –80 kg/adt (calculated as active chlorine) at a temperature below 90°C and to bring the delignification process substantially to its end in less than ten minutes, preferably in a few minutes. In other words, compared with the kinetic model referred to above, only about one tenth of the time given in the model is needed for the reaction. In practice this can be transferred directly to the size of the reaction vessel, which may possibly be only a tube reactor instead of a large tower used today.

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25 According to a preferred embodiment of the invention, a probe measuring the chemical residue has been provided following the treatment vessel, which in some cases may be only a tube. When the chemical dose has been selected based on the lignin and the brightness indicator of the pulp, the temperature of the process is adjusted based on the residual chemical so that the whole chemical dose is consumed within the treatment time determined by the size of the treatment vessel and the production of the line.

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In the adjustment method described above, the temperature is an active parameter in ensuring the consumption of chemical and in optimizing the treatment time. This can be done in the process according to the present invention because the retention between the mixing of the chemicals and the end of the process is short. As the mixing of chemicals is according to our study an essential part of the process in order to ensure a quick reaction, the process is provided with one or several efficient chemical mixer/s. Thus the chemical may be mixed for example with two mixers disposed one after the other in a tube line.

According to a further embodiment of the present invention, an essential part of the process is to guide the process with the temperature so that the process is in contact with the chemicals only as long as is necessary for the consumption of the bleaching chemical. In the prior art, i.e. in almost all the D_0 stages used in the world, the process conditions have been determined so carefully (mainly according to the kinetic model already referred to earlier in several connections) that all the chemical is consumed much before the top of the tower and what is left at end stage is the reaction products and the pulp treated with the bleaching chemical. This gives a change to pulp quality losses, particularly to decrease of pulp brightness as by-reactions continue for a long time before the pulp bleaching stage ends, i.e. before the pulp arrives to a washer/press. The method according to our invention allows active adjustment of the bleaching reaction to continue during the whole retention of the reactor but prevents it from continuing to a level where the bleaching chemical has already been consumed and the quality losses begin to occur without the positive bleaching effect provided by the bleaching chemical.

Figure 5 illustrates an apparatus according to a preferred embodiment of the invention for performing a chlorine dioxide bleaching stage D_0 . It comprises a high-intensity, preferably a so-called fluidizing mixer 30, by means of which chlorine dioxide and if necessary either oxygen or alkali is mixed into the pulp in order to adjust the pH. Close to the mixer 30 in connection with the D_0 stage, preferably prior to the mixer 30, a heater has been provided, which may be for example a direct or an indirect steam heater 32 or a liquid - liquid heater. After the chemical mixing and the heating, the pulp is guided to a reaction vessel, i.e. a treatment tower 34. After the tower 34, residual chlorine dioxide is determined from the pulp by a residue measurement, based on which it is possible, and in

fact the intention, in this embodiment of the invention to adjust the temperature of the pulp, if necessary, preferably before the pulp is fed to the first mixer 30. If dioxide remains in the pulp after the reaction vessel 34, the temperature is raised by the heater 32 and, after the retention of the treatment stage, it is checked if there still is dioxide left in the pulp. On the other hand, if all the dioxide has been consumed the temperature may be decreased in order to increase the treatment time. By this measure it can be ensured that the whole treatment time is used in a beneficial bleaching reaction. At the same time, the time is minimized during which the pulp is in contact with the reaction products. From the residue measurement 36 the pulp flows in this embodiment to another mixer 38, in which a new dose of chlorine dioxide is mixed and, if necessary, chemical needed for the adjustment of the pH. Another heater 40 has been provided in connection with the mixer 38, by means of which the temperature of the second step may be raised, if necessary. After this the pulp is guided to another treatment vessel or tower 42 and from there further to a washer 44.

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According to a preferred method, the dioxide residue is measured by selecting a small dioxide amount in a way as the target value towards which the process is adjusted. Because of the corrosion risk the monitoring of the residual volume is of vital importance in order to ensure adequate life of the equipment. Then the value guiding the adjustment is the relative residue, i.e. the difference between the target value and the measured value.

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In addition to the steam heating methods described above of heating the pulp close to the chemical mixing with low-pressure steam before the pulp is pumped to the bleaching stage, the heating may be performed also by heating the diluting filtrate or by heating the displacing wash liquid of the previous washer. All these methods give a similar result if the temperature measurement has been arranged and connected to the control circuit. Thus the heating method is not essential, but the adjustment of the temperature must be active and the temperature must be adjustable within a certain range. Thus the adjustment based on the information from the residue measurement may be adjustment of the volume of the steam used as the heat source, adjustment of the heating of the filtrate used for dilution or adjustment of the heating of the wash liquid of the washer.

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Some kind of a processor is preferably connected with the apparatus described above and in particular with the adjustment system used in connection with it, although also manual adjustment can be used, to guide for example the volume of steam flowing into the heater 32 based on the residual chlorine dioxide. At least two adjustment methods are thinkable.

- 5 According to the first method, the amount of chlorine dioxide in the treated pulp indicated by the residue measurement only guides more efficiency to the heating of the pulp, for example more steam to the heater. It is advantageous to add a retention connection with the system so that a dioxide finding in the residue measurement immediately causes a certain raise in the heating efficiency which is kept constant at least for the time the
- 10 bleaching process takes so that the change caused by the heating has time to arrive to the residue measurement. After this the result of the residue measurement is reassessed and the necessary changes are made in the heating efficiency.

- The second method is actually a continuation of the previous one in that sense that by
- 15 adding some logic to the adjustment system, it is possible to "teach" the system to adjust itself optimally. In other words, when the system looks for the optimal increases in the heating efficiency in relation to the chlorine dioxide residue the way described above, the "correct" pairs of chlorine dioxide residues and efficiency increases may be saved in the memory of the processor, whereby the adjustment system can in continuous operation
- 20 adjust the heating quickly without "searching". Naturally, in the "teaching phase" the increases in the heating efficiency should be made in relatively small steps. Then there is no risk of having raised the temperature too quickly, which would result in the bleaching reaction coming to its end too early and the pulp having too much time to start reacting with the reaction products of the bleaching reaction.

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- Further it is possible, if so desired or based on further tests considered necessary, to take into consideration in the adjustment logic also the pulp temperature. In other words, the increase in the heating efficiency would not be directly dependent on the chlorine residue, only, but to some extent also for example on the temperature of the pulp after the
- 30 temperature adjustment or the temperature at the residue measurement.

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- When the process apparatus described above is desired to be used as optimally as possible it works so that so much chlorine dioxide is dosed to the first treatment step, i.e. to the mixer 30, that its consistency in the fiber suspension becomes less than 2.5 g/l, preferably 2.9 g/l calculated as active chlorine. In most cases this dose can be performed by
- 5 calculating in relation to the pulp flow as the travel of chlorine dioxide counter-currently from the filtrates obtained from wash stages subsequent to the process is prevented. The bleaching stage tower is used, in the process sense, to refer to the retention taking place after the mixing, which retention may also be realized for example by a tube or an enlargement of a tube. The bleaching stage and the retention after it have been
- 10 dimensioned in the process for a certain production whereby the residue measurement has been provided, in view of the adjustability of the process, advantageously in the discharge of the pulp; based on the measurement the heating of the pulp prior to feeding of it to the reaction vessel and the amount of chlorine dioxide to be fed may be controlled so that the residue remains, according to one way of operation, practically at zero. According to
- 15 another way of operation, the temperature of the pulp to be fed to another mixer is adjusted based on the residue measurement at the discharge of the tower so that if some unreacted dioxide has remained in the pulp in the first tower, the residue after the second tower does not remain detrimentally high.
- 20 Figure 6 illustrates a bleaching apparatus according to yet another preferred embodiment of the invention. The embodiment of Figure 6 differs from the one in Figure 5 in fact only in that in the embodiment illustrated in Figure 6 the process apparatus comprises three subsequent treatment towers. The apparatus embodiment depends mainly on the fact that it may be necessary in the D_0 stage to reduce the Kappa number, i.e. the lignin
- 25 content of the pulp more than can be achieved in two towers using the low dioxide contents of the invention. Then it is sensible to divide the dioxide dose into three substantially equal portions so that the dioxide content in each tower remains under the limit value given above and on the other hand the chemical consumption is even.
- 30 Naturally it is clear that at its simplest many of the advantages of the invention are achievable already with apparatus, which comprises from the apparatus illustrated in figure 5 only the first reaction vessel 34 with its pulp dilution and heating apparatus 32,

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chemical feed apparatus 30, residual dioxide measurement 36 and wash apparatus 44. Even with this apparatus the pulp treatment time with chlorine dioxide can be optimized so that the pulp does not stay too long in contact with the reaction products.

- 5 Thus it is clear that the bleaching process according to the invention may be adapted to the required decrease in Kappa number merely by changing the number of treatment towers. It should be noted that even if this seems now to be a solution involving expensive apparatus, it is quite the opposite. If the initial situation is that prior art dioxide treatments require treatment times of 0.5 - 1 hour, they have to be performed in large
- 10 bricked bleaching towers. A bricked tower instead of an ordinary metal tower is required because of the strong corrosive influence of chlorine dioxide. Now, when treatment times of only of the order of 1 - 10 minutes are required, a substantially smaller treatment vessel is required, which may be even a glass fiber or standard tube vessel, which is small compared with the conventional towers, and the manufacturing costs as well as
- 15 construction, erection, isolation and instrumentation costs of it are only a fraction of those of the corresponding prior art bricked towers.

When the reactions of the pulp can be arranged to take place practically in one closed space up to the wash apparatus, the process eliminates gaseous emissions; thus no gas

20 emission collecting devices used in conventional stages are needed. This saves investment costs and is also advantageous in view of the climate protection.

As can be understood from the above description, a new chlorine dioxide bleaching method avoiding the drawbacks and problems of prior art methods and apparatus has been

25 developed, the characteristic features of which are disclosed in the appended claims. Thus it is clear that only a few preferred embodiments of the invention have been described above, which in no way intend to limit the scope of protection of the invention from what is defined by the patent claims.